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**(54) IDONITRILES AS CHAIN TRANSFER AGENTS IN THE MANUFACTURE OF
PERFLUOROPOLYMERS**

**JOD-ENTHALTENDE NITRILE ALS KETTENÜBERTRAGER ZUR HERSTELLUNG VON
PERFLUOROPOLYMEREN**

**IDONITRILES UTILISES COMME AGENTS DE MIGRATION DE CHAÎNE DANS LA FABRICATION
DE PERFLUOROPOLYMERES**

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(73) Proprietor: **E.I. DU PONT DE NEMOURS AND
COMPANY**
Wilmington Delaware 19898 (US)

(72) Inventors:
• **HUNG, Ming-Hong**
Wilmington, DE 19803-2202 (US)

- **LOGOTHETIS, Anestis, Leonidas**
Wilmington, DE 19810-3430 (US)
- **YANG, Zhen-Yu**
Wilmington, DE 19810-2403 (US)

(74) Representative: **Jones, Alan John et al**
CARPMAELS & RANSFORD
43 Bloomsbury Square
London, WC1A 2RA (GB)

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US-A- 4 089 804 **US-A- 5 504 248**

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Description**FIELD OF THE INVENTION**

- 5 [0001] The use of fluorinated iodonitriles as chain transfer agents in the free radical polymerization of vinyl monomers to form perfluoropolymers is disclosed.

TECHNICAL BACKGROUND

- 10 [0002] The free radical (catalyzed) polymerization of perfluorovinyl monomers to perfluorinated polymers (both plastics and elastomers) is a well known process, see for instance U.S. Patents 3,132,123, 3,467,638, 3,682,872, 4,948,853, 4,973,634, and 4,983,697, and H. Mark., et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd. Ed., Vol. 16, John Wiley & Sons, New York, 1989, p. 577-648. In such a polymerization the monomer(s) is (are) contacted with a free radical initiator and the polymerization is allowed to proceed. Such polymerizations are often carried out in solution, aqueous suspension or emulsion, or by other means. Perfluorinated plastics are useful in many applications wherein high temperature resistance and/or good chemical resistance are important. Perfluoroelastomers are useful in similar applications wherein elastomeric properties are desired, as in various types of seals such as o-rings, chevron rings, shaft seals, and valve packing and washers.

- 15 [0003] In making these polymers for various applications it is often desirable to control the molecular weight, particularly to decrease the molecular weight from that which would be obtained in the absence of chain transfer agents. Lower molecular weight polymers often are easier to process, i.e., form into useful shapes. If the polymer is to be crosslinked, it is preferred that any chain transfer agent that is used contain functional groups such that end groups of the polymers, which are mostly formed by a chain transfer reaction involving the chain transfer agent, contain functional groups which may act as crosslinking sites (sometimes also called curesites). By reacting the chain ends, crosslinked networks with better physical properties are often obtained.

- 20 [0004] One useful type of chain transfer agent in such polymerizations is fluorinated alkyl iodides, especially fluorinated alkyl diiodides. When an alkyl diiodide causes a chain transfer reaction to occur, both chain ends that form contain iodine, which may be used as a curesite to crosslink the polymer. However, these diiodides, and/or byproducts produced in their syntheses are often quite toxic, thereby requiring extra precautions (and expense) in their manufacture and use. Less toxic substitutes that perform the chain transfer function, and which provide curesites at chain ends, are therefore desirable. The use of such iodides as chain transfer agents is reported in U.S. Patents 4,000,356, 4,243,770, 30 4,361,678, 4,948,852, 4,948,853, 4,973,633, 4,973,634, and 4,983,697. None of these patents describe the use of the chain transfer agents described herein.

35 **SUMMARY OF THE INVENTION**

- [0005] This invention concerns a process for the free radical polymerization of vinyl monomers to produce perfluoropolymers, wherein the improvement comprises, using as a chain transfer agent a compound of the formula I_nR^1CN , wherein:

40 R^1 is perfluoroalkyl having 2 or 3 free valencies or perfluoroalkyl having 2 or 3 free valencies and containing one or more ether oxygen atoms;
 n is 1 or 2;

45 and provided that when n is 1, R^1 has two free valencies, and when n is 2, R^1 has 3 free valencies.

DETAILS OF THE INVENTION

- 50 [0006] In the polymerization process described herein, an iodoperfluoroalkylnitrile is used as a chain transfer agent in the free radical polymerization of vinyl monomers to perfluoropolymers. Thus the vinyl monomers themselves should, for the most part, be perfluorinated so as to produce a perfluoropolymer. It is preferred that the perfluoropolymer produced is a perfluoroelastomer. By a perfluoroelastomer is meant a polymer whose glass transition temperature and melting point (if any) are below about 35°C, preferably below about 25°C.

- 55 [0007] Useful monomers in this process include perfluoroolefins such as tetrafluoroethylene (TFE), hexafluoropropylene, perfluoro(2,2-dimethyldioxole), and perfluoro(alkyl vinyl ethers) wherein the alkyl group has 1 to 20, preferably 1 to 5, carbon atoms such as perfluoro(methyl vinyl ether) (PMVE), perfluoro(propyl vinyl ether), and $R^3(OR^4)_mOCF=CF_2$ wherein R^3 is perfluoroalkyl containing 1 to 20 carbon atoms, each R^4 is perfluoroalkylene containing 1 to 20 carbon atoms, and m is an integer of 1 to 5, and combinations thereof. A preferred polymer is an elastomeric copolymer of TFE and a perfluoro(alkyl vinyl ether), more preferably a copolymer of TFE and PMVE. Another preferred

copolymer is a copolymer in which at least 40 mole percent of the repeat units are derived from TFE.

[0008] Elastomeric copolymers may also contain (preferably) small amounts (0.1 to 5 mole percent of the repeat units) of curesite monomers. Curesite monomers are polymerizable vinyl monomers that contain functional groups that act as curesites, i.e., take part in any subsequent crosslinking reactions. A preferred curesite monomer contains one or more nitrile groups. Such nitrile containing curesite monomers are disclosed in U.S. Patents 3,561,186 and 4,281,092. A particularly preferred nitrile containing curesite monomer is perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene) (8CNVE). All of these curesite monomers are useful in combination with the (co)polymers mentioned above.

[0009] The chain transfer agents disclosed herein are perfluorinated alkanes containing a nitrile group, one or two iodine atoms, and optionally one or more ether oxygen atoms. These compounds have the formula $I_n R^1 CN$, wherein n and R^1 are as defined above. It is preferred that n is one. In that case R^1 has two free valencies. By a free valence is meant a bond to which either an iodine or the nitrile group is bound to a carbon atom. The nitrile group and the iodine atom(s) may be bound to the same or different carbon atoms. The preparation of idonitriles containing one iodine atom is described in the Experiments herein, and analogous methods may be used to prepare similar compounds. Idonitriles containing one or two iodine atoms can also be made by methods described in U.S. Patent 5,504,248, which is hereby included by reference.

[0010] It is preferred that R^1 has 1 to about 50 carbon atoms, more preferably 2 to about 20 carbon atoms. Preferred groups for R^1 are $-(CF_2)_m-$ wherein m is 1 to 20, especially preferably when m is 1 or 2, CF_3CF_2- , CF_2- and $-CF_2CF(CF_3)OCF_2CF_2-$. Preferred iodoperfluoronitriles are $I(CF_2)_mCN$ wherein m is 1 to 20, especially when m is 1 or 2, $CF_3CF_2CF_2CN$, $CF_3CF(CN)I$, and $ICF_2CF(CF_3)OCF_2CF_2CN$.

[0011] Polymerizations using the above chain transfer agents may be run in any of many known ways. The polymerizations may be continuous, semi-batch or batch processes. They may be run as aqueous emulsions or suspensions, or organic solutions or suspensions. Typical amounts of monomers, free radical initiators, surfactants (if present), and monomers are used under the usual conditions under which these polymers are made.

[0012] When the iodoperfluoroalkylnitriles are used as chain transfer agents, and when chain transfer takes place, it is believed that one of the chain ends formed contains an iodine atom and the other chain contains a nitrile group (and may also contain an iodine atom if a diiodoperfluoroalkylnitrile is used). Both iodides and nitriles may take part in suitable crosslinking reactions, see for instance U.S. Patents 4,983,697 and 5,447,993. Therefore, of course, the polymer formed in the polymerization process may be crosslinked.

[0013] In the Experiments and Examples, all pressures below atmospheric pressure are absolute pressures, while all pressures above atmospheric pressure are gauge pressures.

[0014] In the Experiments and Examples, the following abbreviations are used:

8CNVE - perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene)

APS - ammonium persulfate

Diak® 7 - triallyl isocyanurate available from E. I. du Pont de Nemours and Company, Wilmington, DE, U.S.A.

GC - gas chromatography

Krytox® 16350 - polyperfluoropropylene oxide available from E. I. du Pont de Nemours and Company, Wilmington, DE, U.S.A.

Luperco® 101XL - 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane available from Pennwalt Corporation, Lucidol Division.

PMVE - perfluoro(methyl vinyl ether)

TFE - tetrafluoroethylene

TPT-OH - triphenyltin hydroxide

[0015] In the Examples, polymers were tested using the following ASTM tests:

Oscillating Disc Rheometer (ODR) - D2084

Mooney Scorch - D1646

Tensile Properties, O-rings - D1414

Compression Set, O-rings - D1414

Experiment 1

Preparation of 2-Iodo-1,1,2,2-tetrafluoroethyl Fluorosulfate ($ICF_2CF_2OSO_2F$)

[0016] Into a 1-liter pressure reactor was charged a mixture of iodine monochloride (162.5 g, 1.0 mol) and fluorosulfonic acid (110 g, 1.1 mol). The reactor was cooled and tetrafluoroethylene (120 g, 1.2 mol) was added. After the addition of TFE was complete, the reaction mixture was heated at 100°C for 10 hr. The cooled mixture was then slowly poured into a large amount of ice with stirring. The lower layer was separated, washed with dilute $NaHSO_3$ solution

and water and dried over MgSO_4 . Distillation afforded the desired product as a clear liquid (215 g, 66% yield), bp. 87-88°C. ^{19}F NMR (188.24 MHz, CDCl_3): -85.4 (dt, $J = 8.4$ Hz, $J = 5.2$ Hz, 2F), -65.7 (t, $J = 5.2$ Hz, 2F), +49.6 (t, $J = 8.3$ Hz, 1F).

5 Experiment 2

Preparation of 2-Iodo-1,1,2,2-tetrafluoroethyl Chlorosulfate ($\text{ICF}_2\text{CF}_2\text{OSO}_2\text{Cl}$)

10 [0017] Into a 1-liter pressure reactor was charged a mixture of iodine monochloride (390 g, 2.4 mol) and chlorosulfonic acid (490 g, 4.206 mol). The reactor was cooled and kept at 0-10°C until 300 g of tetrafluoroethylene (3.0 mol) was added. After the addition of TFE was complete, the reaction mixture was held at 0-10°C for 6 hr, at 25°C for 2 hr and at 50°C for 2 hr. The reaction mixture was then slowly poured into a large amount of ice with stirring, and worked up as described above. The desired product was obtained (610 g, 74% yield), bp. 62-64°C/6.7 kPa. ^{19}F NMR (188.24 MHz, CDCl_3): -85.6 (t, $J = 4.5$ Hz, 2F), -65.3 (t, $J = 4.5$ Hz, 2F). Anal. Calcd. for $\text{C}_2\text{F}_4\text{IClSO}_3$: C: 7.02, F: 22.19; Found: 15 C: 7.19, F: 22.73.

Experiment 3

20 Preparation of Ethyl Iododifluoroacetate ($\text{ICF}_2\text{CO}_2\text{Et}$)

[0018]

(a) From 2-iodo-1,1,2,2-tetrafluoroethyl chlorosulfate

25 A 500 mL flask was charged with sodium fluoride (18.9 g, 0.45 mol) and ethanol (200 mL) and cooled in an ice-water bath. 2-Iodo-1,1,2,2-tetrafluoro-ethyl chlorosulfate (103 g, 0.3 mol) was added slowly. The reaction was exothermic and the reaction temperature was maintained at 20-30°C. After addition, the reaction mixture was stirred at room temperature for 10 hr and then poured into cold water. Ether was added to extract the product. The organic layer was washed with saturated NaCl solution and dried over MgSO_4 . Evaporation of the solvent *in vacuo* followed by distillation gave the ethyl iododifluoroacetate (68.1 g, 91 % yield), bp. 57-58°C/4.0 kPa. ^1H NMR (300 MHz, CDCl_3): δ 1.35 (t, $J = 7.0$ Hz, 3H), 4.37 (q, $J = 7.0$ Hz, 2H). ^{19}F NMR (188.24 MHz, CDCl_3): -57.9 (s, 2F).

30 (b) From 2-iodo-1,1,2,2-tetrafluoroethyl fluorosulfate

Ethyl iododifluoroacetate (73.4 g, 74% yield) could also be prepared from 2-iodo-1,1,2,2-tetrafluoroethyl fluorosulfate (130.4 g, 0.4 mol), potassium fluoride (23.2 g, 0.4 mol) and ethanol (150 mL) according to the procedure described in Experiment (3a).

35 Experiment 4

Preparation of Iododifluoroacetamide ($\text{ICF}_2\text{CONH}_2$)

40 [0019]

(a) From 2-iodo-1,1,2,2-tetrafluoroethyl chlorosulfate

45 Into a stirred solution of ammonium hydroxide (150 mL, 28-30% in aq.) and ether (150 mL) was added dropwise $\text{ICF}_2\text{CF}_2\text{OSO}_2\text{Cl}$ (102.8 g, 0.3 mol) with external cooling. The temperature was maintained at 10-20°C during the addition. After that, the mixture was warmed to room temperature and stirred for 30 min. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with brine and dried over MgSO_4 . Evaporation of the solvent followed by recrystallization from hexane/ether gave $\text{ICF}_2\text{CONH}_2$ (61.5 g, 92% yield) as a white solid, mp. 96-98°C. ^1H NMR (300 MHz, acetone- d_6): δ 7.35 (br, 1H), 7.81 (br, 1H). ^{19}F NMR 188.24 MHz, 300 MHz, acetone- d_6): -57.5.

50 (b) From 2-iodo-1,1,2,2-tetrafluoroethyl fluorosulfate

Iododifluoroacetamide (28.5 g, 86%) could be prepared from $\text{ICF}_2\text{CF}_2\text{OSO}_2\text{F}$ (48.9 g, 0.15 mol), ammonium hydroxide (80 mL, 28-30% in aq.) and ether (100 mL) in a similar way as described in Experiment (3a).

(c) From ethyl iododifluoroacetate

55 Ammonia gas was bubbled slowly into a stirred solution of $\text{ICF}_2\text{CO}_2\text{Et}$ (62.5 g, 0.25 mol) and ether (150 mL) with ice water bath cooling. The reaction was monitored by GC for the complete conversion of the starting material. After usual the workup, $\text{ICF}_2\text{CONH}_2$ was obtained in almost quantitative yield (55 g).

Experiment 5Preparation of Iododifluoroacetonitrile (ICF_2CN)

5 [0020] Iododifluoroacetamide (155 g, 0.7 mol) was well mixed with P_2O_5 (100 g, 0.704 mol) and heated at 150°C in vacuo (about 20 kPa). The volatile was collected in a cold trap (dry ice-acetone bath). The heating oil bath temperature was increased slowly to 200°C and the reaction was stopped until no more product was distilled off. Redistillation gave pure ICF_2CN (115 g, 81% yield), b.p. $52\text{--}54^\circ\text{C}$. ^{19}F NMR (188.24 MHz, CDCl_3): -46.5 . MS: Calcd. for $[\text{M}^+]$: 202.9116; Found: 202.9116.

Experiment 6Preparation of $\text{I}(\text{CF}_2\text{CF}_2)_n\text{OSO}_2\text{F}$ Oligomer

15 [0021] 2-Iodo-1,1,2,2-tetrafluoroethyl fluorosulfate (65.2 g, 0.2 mol) was mixed with TFE (25 g, 0.25 mol) in a sealed stainless tube. The mixture was heated at 250°C for 4 hr. The product was unloaded and subjected to fractional distillation. About 25 g (38.3%) of the starting was recovered. Other oligomeric products (ca. 50 g) obtained were $\text{I}(\text{CF}_2\text{CF}_2)_2\text{OSO}_2\text{F}$, b.p. $42^\circ\text{C}/3.3$ kPa, $\text{I}(\text{CF}_2\text{CF}_2)_3\text{OSO}_2\text{F}$, b.p. $54^\circ\text{C}/700$ Pa, and higher boiling $\text{I}(\text{CF}_2\text{CF}_2)_n\text{OSO}_2\text{F}$ ($n > 3$). For $\text{I}(\text{CF}_2\text{CF}_2)_2\text{OSO}_2\text{F}$: ^{19}F NMR (188.24 MHz, CDCl_3): -60.3 (t, $J = 13.8$ Hz, 2F), -83.7 (d, $J = 7.2$ Hz, 2F), -113.7 (s, 2F), -124.1 (t, $J = 12.4$ Hz, 2F), $+50.9$ (m, br, 1F); Mass. Calcd. for $[\text{M}^+]$: 425.8471; Found: 425.8381. For $\text{I}(\text{CF}_2\text{CF}_2)_3\text{OSO}_2\text{F}$: ^{19}F NMR (188.24 MHz, CDCl_3): -59.7 (m, 2F), -83.5 (m, 2F), -113.5 (m, 2F), -121.4 (m, 2F), -122.3 (m, 2F), -125.0 (m, 2F), $+50.6$ (t, $J = 8.2$ Hz, 1F); Mass. Calcd. for $[\text{M}^+]$: 525.8407; Found: 525.8345.

Experiment 7Preparation of 2-Iodoheptafluoropropyl Fluorosulfate ($\text{CF}_3\text{CFICF}_2\text{OSO}_2\text{F}$)

25 [0022] Into a 1.3-liter stainless steel tube was charged a mixture of iodine monochloride (130 g, 0.80 mol) and fluorosulfonic acid (88 g, 0.88 mol). The tube was sealed and cooled, then hexafluoropropylene (144 g, 0.96 mol) was transferred into the tube. The reaction mixture was kept at 25°C for 2 hr, 50°C for 2 hr and 80°C for 4 hr. The product was unloaded from the shaker tube and poured into ice water. The bottom organic layer was separated, washed with water and distilled to afford the title product (120 g, 40% yield) as a clear liquid, b.p. $47^\circ\text{C}/6.7$ kPa. ^{19}F NMR (188.24 MHz, CDCl_3): -74.5 (m, 3F), -77.0 (m, AB-pattern, 2F), -148.2 (m, 1F), $+49.7$ (m, 1F).

Experiment 8Preparation of 2-Iodotetrafluoropropionamide ($\text{CF}_3\text{CFICONH}_2$)

35 [0023] Into a glass flask was placed a mixture of aqueous ammonium hydroxide (28 wt. %, 40.5 mL, 0.6 mol) and methylene chloride (80 mL) which was cooled to $10\text{--}15^\circ\text{C}$. 2-Iodoheptafluoropropyl fluorosulfate from Experiment 7 (37.6 g, 0.1 mol) was added slowly with vigorous stirring while the reaction temperature was kept at $< 15^\circ\text{C}$. After addition, the mixture was warmed to ambient temperature, the bottom organic layer was separated, washed with aqueous sodium bisulfite solution, dried over MgSO_4 . The solvent was removed *in vacuo* to give the title product as a white solid (18.5 g, 68.3% yield), mp. $75\text{--}77^\circ\text{C}$, ^1H NMR (300 MHz, CDCl_3): δ 6.98, 6.53 (2 broad singlets); ^{19}F NMR (188.24 MHz, CDCl_3): -76.3 (2 singlets, 3F), -138.5 (m, 1F); IR: 1690 cm^{-1} (C=O); Anal. Calcd. for $\text{C}_3\text{H}_2\text{F}_4\text{INO}$: C: 13.30, H: 0.74, F: 28.05, N: 5.17. Found: C: 13.68, H: 0.83, F: 28.43, N: 5.21. Mass. Calcd. for $[\text{M}^+]$: 270.9117; Found: 270.9093.

Experiment 9Preparation of 2-Iodotetrafluoropropionitrile (CF_3CFICN)

50 [0024] 2-Iodotetrafluoropropionamide prepared from Experiment 8 (16.3 g, 0.06 mol) was mixed well with P_2O_5 (16.3 g, 0.115 mol) in a flask under nitrogen atmosphere. The mixture was heated slowly to 95 to 100°C , a volatile product started to form and was collected in a cold trap (dry ice-acetone bath). The title product was obtained as a slightly pink liquid after purification by distillation, yield 12.5 g (82.5%), b.p. $68\text{--}70^\circ\text{C}$. ^{19}F NMR (188.24 MHz, CDCl_3): -78.7 (2 singlets, 3F), -137.9 (q, $J = 16$ Hz, 1F); IR: 2288 cm^{-1} ($\text{C}\equiv\text{N}$); Mass. Calcd. for $[\text{M}^+]$: 252.9382; Found: 252.9012.

Experiment 10

Preparation of 2-Iodotetrafluoropropanoamide

- 5 **[0025]** A 1 L autoclave was charged with 353 g iodine and 285 g of trifluoromethoxypentafluorocyclopropane and heated at 150°C for 3 h and then 240°C for 12 h. After the autoclave was cooled to room temperature, the reaction mixture was diluted with 1 L of ether and cooled to -78°C. Ammonia gas was added until the solution was basic. The reaction mixture was warmed to room temperature over 1.5 h. The mixture was poured into 1 L of ether and washed with water and dried over MgSO_4 . After removal of the ether, 203.5 g of product was obtained. An analytical sample
- 10 was obtained by recrystallization from hexane and ether, mp 136-137°C. ^{19}F NMR: -62.3 (t, J = 5 Hz, 2F), -112.1 (t, J = 5 Hz, 2F). ^1H NMR (Acetone- d_6): 7.99 (br, 1H), 7.69 (br, 1H). IR (neat): 3375, 3267 (m), 3193 (m), 1708 (s), 1416 (s), 1180 (s), 1080 (s), 647 (s). Anal: Calcd for $\text{C}_3\text{H}_2\text{F}_4\text{NOI}$: C, 13.30; H, 0.74; F, 28.05; N, 5.17; I, 46.84. Found: C, 13.35; H, 0.78; F, 27.10; N, 4.81; I, 46.87.

15 Experiment 11

Preparation of Iodotetrafluoropropanonitrile

- 20 **[0026]** A mixture of 150 g of fine powder of $\text{ICF}_2\text{CF}_2\text{CONH}_2$ and 235 g of P_2O_5 was heated at 130 to 150°C, during which time volatiles were distilled out. Final volatiles were collected in a -78°C trap at 26.6 kPa. A total of 125.3 g of crude product was obtained, 95% pure by GC. Redistillation gave pure product, bp 60-61 °C. ^{19}F NMR: -63.3 (t, J = 10.4 Hz, 2F), -100.5 (t, J = 10.4 Hz, 2F). IR (neat): 2264 (w), 1235 (s), 1196 (s), 1172 (s), 1146 (s), 1089 (s), 1065 (s), 893 (s).

25 Experiment 12Preparation of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CONH}_2$

- 30 **[0027]** To a stirred solution of 22.5 g of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CONH}_2$ and 30 mL of CH_2Cl_2 was added 3 g of NH_3 through a dry ice condenser which was at room temperature. After the addition was complete the reaction mixture was stirred at room temperature overnight. After removal of volatiles, 21.6 g of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CONH}_2$ were obtained. ^1H NMR: 6.40 (br, 1H), 6.65 (br, 1H). ^{19}F NMR: -58.3 (dm, J = 212 Hz, 1H), -60.0 (dm, J = 212 Hz, 1F), -76.7 (m, 3F), -82.1 (dm, J = 139.5 Hz, 1F), -83.5 (dm, J = 139 Hz, 1F), -123.1 (s, 2F), -134.1 (m, 1F). IR: 3413 (s), 1697 (s), 1230 (s).
- 35

Experiment 13Preparation of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$

- 40 **[0028]** A mixture of 17.5 g of fine powder of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CONH}_2$ and 17 g of P_2O_5 was heated at 150 to 200°C, during which volatiles were distilled out. Final volatiles were collected in a -78°C trap at 13.3 kPa. A total of 13.8 g of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ were obtained, 95% pure by GC. ^{19}F NMR: -58.6 (dm J = 212.4 Hz, 1F), -60.1 (dm J = 212 Hz, 1F), -76.7 (m, 3F), -83.3 (dm, J = 135 Hz, 1F), -84.8 (dm, J = 135 Hz, 1F), -108.6 (t, j = 6.3 Hz, 2F), -133.6 (m, 1F). IR (neat): 2268 (m), 1113 (s).
- 45

Example 1

- 50 **[0029] Batch Polymerization:** Into a 400 ml shaker tube were placed 200 ml of water, 7 g of perfluorooctanoic acid ammonium salt, 0.5 g of disodium hydrogen phosphate heptahydrate, 3 g of perfluoro-(8-cyano-5-methyl-3,6-dioxo-1-octene), 0.1 g of ammonium persulfate and 0.2 g of 1-iodo-2-cyano-perfluoroethylene. The shaker tube was cooled at -30 to -40°C, evacuated and 35 g of tetrafluoroethylene and 60 g of perfluoro(methyl vinyl ether) were condensed in the shaker tube. The tube was sealed and allowed to warm to 70°C while shaking. The reaction was followed by pressure drop and after 4 h it was stopped. The polymer was isolated by adding the stable polymer emulsion to a 4 wt % solution of magnesium sulfate in water at 90°C. The polymer precipitated as crumb and it was washed with copious
- 55 amounts of water before drying in an oven at 70°C. The polymer from four identical runs was combined and weighed 165 g. The properties are described in Table 1.

[0030] This polymer was compounded on a rubber mill using a dual cure system (peroxide, triallyl isocyanurate and triphenyl tin hydroxide, see U.S. Patent 5,447,993) in the formulation shown in Table 1. O-Rings were pressed on a

hydraulic press at 175°C and 3.5 MPa pressure using a proper mold. The crosslinked parts were post-cured and the properties are shown in Table 1.

TABLE 1

TFE/PMVE/8CNVE TERPOLYMER MODIFIED WITH ICF ₂ CF ₂ CN	
POLYMER	
PMVE WT%	37.4
8CNVE WT%	1.6
IODINE WT %	0.14
MELT INDEX, g/10 min	
250°C	57.0
200°C	13.1
Mooney Viscosity at 121°C D1646	< 30
Inherent Viscosity	.217
FORMULATION	
POLYMER	100
MT BLACK	10
KRYTOX® 16350	10
LUPERCO® 101XL	2
DIAK® 7	2
TPT-OH	2
ODR 177°C/3° ARC	
ML, Nm	.56
ts ₂ min	1.5
MH, Nm	4.3
MH-ML, Nm	3.7
TC70, min	4
PROPERTIES (O-rings)¹	
M ₁₀₀ , MPa	9.8
Tb, MPa	17.0
Eb, %	173
Comp. Set 204°C/70h	29

¹ Samples were press-cured at 175°C/20 min and post-cured at 305°C for 18 h under nitrogen

Example 2

[0031] Continuous Polymerization: The polymerization process is essentially the same described in U.S. Patent 4,983,697. The polymer was prepared in a 2 L mechanically stirred, water jacketed, stainless-steel autoclave operated continuously at 90°C and 6.2 MPa into which was pumped at a rate of 550 ml/h an aqueous polymerization medium/initiator solution comprising of 16 L of water, 55 g of ammonium persulfate, 471 g of disodium hydrogen phosphate heptahydrate, 283 g of ammonium perfluorooctanoate ("Fluorad" FC-143 from 3M Co.). At the same time a separate solution of perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene) (8CNVE), 6.2 g/h, and 1-iodo-2-cyanotetrafluoroethane, 0.2 g/h, were added. A gaseous stream of tetrafluoroethylene (113 g/h) and perfluoro(methyl vinyl ether) (PMVE, 130 g/h) were fed into the reactor at a constant rate by means of a diaphragm compressor. The polymer was continuously removed by means of a let-down valve and unreacted monomers were vented. The latex from 27.6 h was combined and the polymer was coagulated by adding into a hot (90-95 °C) magnesium sulfate heptahydrate solution of about 3700 g in 80 L of water. The coagulated crumb was repeatedly washed with fresh water and dried at 80°C in an air oven. The polymer weighed approximately 3600 g. The properties of the polymer are shown in Table 2.

TABLE 2

ICF ₂ CF ₂ CN MODIFIED TFE/PMVE/8CNVE - POLYMERIZATION			
Polymerization		Results	
Temp.	85°C	PMVE conv. %	60.6
Pressure, MPa	6.2	PMVE % in polymer	42.8
PMVE/TFE Feed ratio	1.15	8CNVE % in polymer	2.2
TFE+PMVE/8CNVE feed ratio	34	Iodine % in polymer	0.02
TFE+PMVE/APS	258	Mooney D1646	
APS/ICF ₂ CF ₂ CN	3.75	121 °C	68
		150°C	24
		Melt Index at 250°C	
		g/10 min	26.8
		Inh. visc.	0.46

[0032] Milling, compounding and crosslinking was done using a dual system of peroxide/triallyl isocyanurate and triphenyl tin hydroxide (TPT-OH)(A), and also using a peroxide cure system (B). The compounding was done a standard rubber mill and O-rings were crosslinked by pressing them in a proper mold at 175 °C/30 min under 3.5 MPa pressure. The physical properties are shown in Table 3.

TABLE 3

ICF ₂ CF ₂ CN MODIFIED TFE/PMVE/8CNVE - PHYSICAL PROPERTIES		
	A (Dual Cure)	B (Peroxide)
Polymer	100	100
MT Black	30	30
Krytox® 16350	10	10
TPT-OH	1	----
Luperco® 101:XL	1	1
Diak® 7	1	1
ZnO	2	2
ODR 190°C/3° Arc		
Minimum, Nm	.56	.56
ts ₂ , min	1.3	1.5
MH, Nm	4.1	2.6
MH-ML, Nm	3.6	2.0
Mooney Scorch at 121°C		
Minimum	47	57
2 pt. rise, min	---	8
After 30 min	47	64
Tensiles (O-rings)		
M50, MPa	3.47	3.11
M100, MPa	6.72	6.85
Tb, MPa	9.83	11.7
Eb, %	148	154
Compression set, 204°C/70 h		
After post-cure	38	42
After Heat Age at 300°C/72 h	57	75

Example 3

[0033] Polymer was prepared as in Example 2, except 0.250 g/h of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$ was used as the chain transfer agent instead of 1-iodo-2-cyanotetrafluoroethane. The polymer properties are shown in Table 4.

[0034] Milling, compounding and crosslinking were done using a TPT cure (A in Table 5) and a dual TPT/peroxide cure (B in Table 5). The compounding was done on a rubber mill and O-rings were crosslinked by pressing them in a mold at 200°C/30 min and post-curing them at 305°C under nitrogen for 42 h. Properties are shown in Table 5.

TABLE 4

PMVE, conv. %	59.6
PMVE, wt. % in polymer	43.2
8-CNVE, wt. % in polymer	1.7
Iodine, wt. %	0.03
inh. visc.	0.50
Mooney viscosity, 150°C	40

TABLE 5

	A	B
Polymer	100	100
MT Black	30	30
Krytox 16350	10	10
TPT	2	2
Diak 7	0.5	1
Luperco 101XL	-	1
Tensiles (O-Rings)		
M50, MPa	2.6	2.6
M100, MPa	6.4	6.7
TB, MPa	10.5	12.2
EB, %	139	146
Compression Set, 204°C/70 h		
After Post-cure	21	21
After Heat-aging, 300°C, 72 h		

Claims

1. A process for the free radical polymerization of vinyl monomers to produce perfluoropolymers, wherein there is used, as a chain transfer agent, a compound of the formula $\text{I}_n\text{R}^1\text{CN}$, wherein:

R^1 is perfluoroalkyl having 2 or 3 free valencies or perfluoroalkyl having 2 or 3 free valencies and containing one or more ether oxygen atoms;

n is 1 or 2;

and provided that when n is 1, R^1 has two free valencies, and when n is 2, R^1 has 3 free valencies.

2. The process as recited in Claim 1 wherein said perfluoropolymer is a perfluoroelastomer.
3. The process as recited in Claim 1 wherein n is 1.
4. The process as recited in Claim 2 wherein n is 1.
5. The process as recited in Claim 1 wherein at least 40 mole percent of repeat units in said perfluoropolymer are derived from tetrafluoroethylene.

6. The process as recited in Claim 4 wherein said fluoropolymer is a polymer of tetrafluoroethylene, hexafluoropropylene, perfluoro(2,2-dimethyldioxole), a perfluoro(alkyl vinyl ether) wherein the alkyl group has 1 to 20 carbon atoms, or $R^3(OR^4)_mOCF=CF_2$ wherein R^3 is perfluoroalkyl containing 1 to 20 carbon atoms, each R^4 is perfluoroalkylene containing 1 to 20 carbon atoms, and m is an integer of 1 to 5, and combinations thereof.
7. The process as recited in Claim 4 wherein said fluoropolymer is a copolymer of a perfluoro(alkyl vinyl ether) and tetrafluoroethylene, wherein said alkyl group has 1 to 5 carbon atoms.
8. The process as recited in Claim 4 wherein said fluoropolymer is a copolymer of perfluoro(methyl vinyl ether) and tetrafluoroethylene.
9. The process as recited in Claim 4 wherein said polymer also contains a repeat unit containing a nitrile group.
10. The process as recited in Claim 8 wherein said polymer also contains a repeat unit containing a nitrile group.
11. The process as recited in Claim 10 wherein said repeat unit containing a nitrile group is derived from perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene).
12. The process as recited in Claim 1 wherein said chain transfer agent is $I(CF_2)_mCN$ wherein m is 1 to 20, CF_3CFICF_2CN , $CF_3CF(CN)I$, or $ICF_2CF(CF_3)OCF_2CF_2CN$.
13. The process as recited in Claim 10 wherein said chain transfer agent is $I(CF_2)_mCN$ wherein m is 1 to 20, CF_3CFICF_2CN , $CF_3CF(CN)I$, or $ICF_2CF(CF_3)OCF_2CF_2CN$.
14. The product of the process of Claim 1.
15. The product of the process of Claim 1 which is crosslinked.
16. The product of the process of Claim 10.
17. The product of the process of Claim 10 which is crosslinked.

Patentansprüche

1. Verfahren zur radikalischen Polymerisation von Vinyl-Monomeren zur Herstellung von Perfluorpolymeren, bei welchem Verfahren als ein Kettenübertragungsmittel eine Verbindung der Formel I_nR^1CN verwendet wird, worin sind:
 R^1 Perfluoralkyl mit 2 oder 3 freien Valenzen oder Perfluoralkyl mit 2 oder 3 freien Valenzen und enthaltend ein oder mehrere Ether-Sauerstoffatome;
n 1 oder 2; und
unter der Voraussetzung, daß R^1 zwei freie Valenzen hat, wenn n 1 ist, und daß R^1 drei freie Valenzen hat, wenn n 2 ist.
2. Verfahren nach Anspruch 1, bei welchem das Perfluorpolymer ein Perfluorelastomer ist.
3. Verfahren nach Anspruch 1, bei welchem n 1 ist.
4. Verfahren nach Anspruch 2, bei welchem n 1 ist.
5. Verfahren nach Anspruch 1, bei welchem mindestens 40 Molprozent Repetiereinheiten in dem Perfluorpolymer deriviert sind von Tetrafluorethylen.
6. Verfahren nach Anspruch 4, bei welchem das Fluorpolymer ein Polymer von Tetrafluorethylen, Hexafluorpropylen, Perfluor(2,2-dimethyldioxol), ein Perfluor(alkylvinylether) ist, wobei die Alkyl-Gruppe 1 bis 20 Kohlenstoffatome hat; oder $R^3(OR^4)_mOCF=CF_2$, worin R^3 Perfluoralkyl mit 1 bis 20 Kohlenstoffatomen ist und jedes R^4 Perfluoralkylen mit 1 bis 20 Kohlenstoffatomen ist und m eine ganze Zahl 1 bis 5; sowie Kombinationen davon.

7. Verfahren nach Anspruch 4, bei welchem das Fluorpolymer ein Copolymer eines Perfluor(alkylvinylethers) und Tetrafluorethylens ist, wobei die Alkyl-Gruppe 1 bis 5 Kohlenstoffatome hat.
8. Verfahren nach Anspruch 4, bei welchem das Fluorpolymer ein Copolymer von Perfluor(methylvinylether) und Tetrafluorethylen ist.
9. Verfahren nach Anspruch 4, bei welchem das Polymer auch eine Repetiereinheit enthält, die eine Nitril-Gruppe enthält.
10. Verfahren nach Anspruch 8, bei welchem das Polymer auch eine Repetiereinheit enthält, die eine Nitril-Gruppe enthält.
11. Verfahren nach Anspruch 10, bei welchem die Repetiereinheit, die eine Nitril-Gruppe enthält, deriviert ist von Perfluor(8-cyan-5-methyl-3,6-dioxa-1-octen).
12. Verfahren nach Anspruch 1, bei welchem das Kettenübertragungsmittel $I(CF_2)_mCN$ ist, worin m 1 bis 20 beträgt: CF_3CFICF_2CN ist; $CF_3CF(CN)I$ oder $ICF_2CF(CF_3)OCF_2CF_2CN$ ist.
13. Verfahren nach Anspruch 10, bei welchem das Kettenübertragungsmittel $I(CF_2)_mCN$ ist, worin m 1 bis 20 beträgt: CF_3CFICF_2CN ist; $CF_3CF(CN)I$ oder $ICF_2CF(CF_3)OCF_2CF_2CN$ ist.
14. Produkt des Verfahrens nach Anspruch 1.
15. Produkt des Verfahrens nach Anspruch 1, wobei das Produkt vernetzt ist.
16. Produkt des Verfahrens nach Anspruch 10.
17. Produkt des Verfahrens nach Anspruch 10, wobei das Produkt vernetzt ist.

Revendications

1. Procédé de polymérisation radicalaire de monomères vinyliques pour produire des perfluoropolymères, dans lequel on utilise, comme agent de migration de chaîne, un composé de formule I_nR^1CN , dans laquelle:
 R^1 est un groupe perfluoroalkyle ayant 2 ou 3 valences libres ou un groupe perfluoroalkyle ayant 2 ou 3 valences libres et contenant un ou plusieurs atomes d'oxygène d'éther;
n vaut 1 ou 2;
et à condition que lorsque n vaut 1, R^1 ait deux valences libres, et lorsque n vaut 2, R^1 ait 3 valences libres.
2. Procédé selon la revendication 1 dans lequel ledit perfluoropolymère est un perfluoroélastomère.
3. Procédé selon la revendication 1 dans lequel n vaut 1.
4. Procédé selon la revendication 2 dans lequel n vaut 1.
5. Procédé selon la revendication 1 dans lequel au moins 40% en moles d'unités répétitives dans ledit perfluoropolymère dérivent du tétrafluoroéthylène.
6. Procédé selon la revendication 4 dans lequel ledit fluoropolymère est un polymère de tétrafluoroéthylène, d'hexafluoropropylène, de perfluoro(2,2-diméthyl-dioxole), un perfluoro(alkylvinyléther) dans lequel le groupe alkyle a 1 à 20 atomes de carbone, ou $R^3(OR^4)_mOCF=CF_2$ où R^3 est un groupe perfluoroalkyle contenant 1 à 20 atomes de carbone, chaque R^4 est un groupe perfluoroalkylène contenant 1 à 20 atomes de carbone, et m est un entier de 1 à 5, et leurs combinaisons.
7. Procédé selon la revendication 4 dans lequel ledit fluoropolymère est un copolymère d'un perfluoro(alkylvinyléther) et de tétrafluoroéthylène, dans lequel ledit groupe alkyle a 1 à 5 atomes de carbone.

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8. Procédé selon la revendication 4 dans lequel ledit fluoropolymère est un copolymère de perfluoro(méthylvinyléther) et de tétrafluoroéthylène.
- 5 9. Procédé selon la revendication 4 dans lequel ledit polymère contient aussi une unité répétitive contenant un groupe nitrile.
- 10 10. Procédé selon la revendication 8 dans lequel ledit polymère contient aussi une unité répétitive contenant un groupe nitrile.
- 10 11. Procédé selon la revendication 10 dans lequel ladite unité répétitive contenant un groupe nitrile dérive du perfluoro (8-cyano-5-méthyl-3,6-dioxa-1-octène).
- 15 12. Procédé selon la revendication 1 dans lequel ledit agent de migration de chaîne est $I(CF_2)_mCN$ où m vaut 1 à 20, CF_3CFICF_2CN , $CF_3CF(CN)I$, ou $ICF_2CF(CF_3)OCF_2CF_2CN$.
- 15 13. Procédé selon la revendication 10 dans lequel ledit agent de migration de chaîne est $I(CF_2)_mCN$ où m vaut 1 à 20, CF_3CFICF_2CN , $CF_3CF(CN)I$, ou $ICF_2CF(CF_3)OCF_2CF_2CN$.
- 20 14. Produit du procédé selon la revendication 1.
- 20 15. Produit du procédé selon la revendication 1 qui est réticulé.
16. Produit du procédé selon la revendication 10.
- 25 17. Produit du procédé selon la revendication 10 qui est réticulé.
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